Atomic Layer Etching
Room Hall 3F - Session ALE-WeA
Modeling in Atomic Layer Etching

Moderators: Steven M. George, University of Colorado at Boulder, **Dmitry Suyatin**, AlixLabs A.B.

1:45pm **ALE-WeA-2 Utilizing Thermodynamic Analysis to Screen Material and Precursor Selection for Selective Thermal Atomic Layer Etching**, ***Landon Keller***, North Carolina State University; *M. McBriarty, B. Zope, M. Moinpour, R. Kanjolia,* Merck KGaA, Darmstadt, Germany; *G. Parsons,* North Carolina State University

Advanced patterning of microelectronic devices requires better understanding and control of chemical mechanisms during atomic scale processing for fabrication of advanced architectures. Thermal atomic layer etching (ALE) is a promising approach to achieve controlled etching and chemical selectivity, but it is not yet widely used in semiconductor manufacturing. To advance ALE, new precursor systems must be identified and discovered to create new viable processed for use in backend applications. In this work, we report a methodology for screening material-precursor systems to be used in ALE using tabulated thermodynamic properties of condensed and gaseous compounds.

Previously, our group developed an ALE process for etching TiO_2 ALD films using WF_6/BCl_3.[1] Using our learning from this process, we performed thermodynamic analysis of Gibbs free energy values and equilibrium compositions using a software package called HSC Chemistry 10.[2] The HSC software generates equilibrium composition diagrams and predicts reactions products in a closed system that can be analyzed through an iterative approach to predict process conditions where reactions should occur thermodynamically and identify conditions for ALE or continuous vapor etch (CVE) across a temperature range. Figure 1a shows that after exposure of TiO_2 to WF_6, solid surface products TiF_4(s) and WO_3(s) are predicted to form from 50°C-195°C. TiO_2 was also exposed to BCl_3 and solid B_2O_3(s) is expected to form across the entire temperature range, as shown in Figure 2b. To mimic an ALE process, the solids formed in Figure 1a were exposed individually to BCl_3 and results are shown in Figures 1c-1d. Solid conversion layers generated on the surface after BCl_3 exposure were next exposed to WF_6 to represent a 2nd ALE cycle. Solid products WO_2Cl_2(s) and B_2O_3(s) were predicted to form and the resulting products after exposure to WF_6(g) are shown in Figures 1e-1f. Figures 1a-1b predict CVE of TiO_2 to occur using WF_6 and not BCl_3 over the temperature range 195°C-400°C. When all the equilibrium species are analyzed together, ALE of TiO_2 is predicted to be possible from 155°C-195°C, with no etching occurring below 155°C. This methodology was repeated with 3 other material systems and their predicted CVE and ALE temperature ranges are shown in Table 1. These results can be compared with experimental data to assess the validity of the predicted temperature ranges.

We believe these findings provide a reliable methodology to predict material-precursor systems for CVE and ALE and will aid with the discovery of new etch systems for atomic scale processing within semiconductor manufacturing.

2:00pm **ALE-WeA-3 Atomistic Surface Processing Simulations: ALE of Transition Metal Dichalcogenides**, ***Suresh Kondati Natarajan***, *N. Pandey, J. Schneider, J. Wellendorff,* Synopsys Denmark ApS, Denmark

Atomic Layer Etching (ALE) is becoming a key thin-film processing technique to enable next-generation semiconductor technology nodes. As ALE employs cyclic processing of materials using sequential self-limiting surface reactions, it can be used in conjunction with atomic layer deposition (ALD) to prepare conformal and smooth nanoscale patterns of extreme limits in semiconductor device fabrication. One of the upcoming ALE applications is preparing CMOS channels based on novel transition metal dichalcogenide (TMD) materials, such as MoS_2, WS_2, $MoSe_2$, and others, which may in time replace silicon. TMDs consist of three atomic planes forming a single layer, and the process to etch TMDs must ensure the removal of the three atomic planes conformally to avoid impurities [1]. The layer-by-layer etching process of TMDs therefore needs special considerations to ensure high conformality, avoid over/under etching of TMD layers, and at the same time provide maximum process capability and yield. In the process of adding or removing surface material atom-by-atom, in-silico atomic-scale modeling approaches are key to understanding mechanisms, finding optimal energies of the reacting species for maximum yield, and predicting process outcomes. Synopsys has developed an industry-grade simulation framework within the Synopsys QuantumATK software [2,3] for atomistic surface processing and have previously demonstrated it for ALD of HfO_2 [4].

In this talk, we will present enhancements of this simulation workflow to simulate ALE processing of TMDs (specifically MoS_2), using sequential Cl_2 plasma exposure and Ar ion bombardment [1]. The simulation workflow involves molecular dynamics simulations with specifically trained machine-learned force fields (ML FFs) and can in principle be applicable to ALE processing of any material.

We will first discuss the simulated saturation profiles of Cl uptake during the Cl_2 plasma pulse along with the trend in the dissociative sticking probability/coverage of Cl_2 molecules as a function of its impact energy. Following that, we will showcase the results for the etch rate during cyclic exposure of Cl_2 plasma and Ar ion along with a list of possible etch by-products. Finally, we will discuss the effect of Ar impact energy and impact angle on the etch rate (yield) at saturated Cl coverage.

[1] K. S. Kim et al., ACS Appl. Mater. Interfaces 9, 11967 (2017).

[2] QuantumATK V-2023.12, Synopsys. (https://www.synopsys.com/silicon/quantumatk.html)

[3] S. Smidstrup et al., J. Phys.: Conden. Matter 32, 015901 (2019).

[4] J. Schneider et al., ALD/ALE 2022, Ghent, Belgium.

2:15pm **ALE-WeA-4 Gas-Phase Etching Mechanism of Amorphous Hydrogenated Silicon Nitride by Hydrogen Fluoride: A Theoretical Study**, ***Khabib Khumaini***, *Y. Kim, R. Hidayat, T. Chowdhury, H. Kim,* Sejong University, Republic of Korea; *B. Cho, S. Park,* Wonik IPS, Republic of Korea; *W. Lee,* Sejong University, Republic of Korea

Understanding the etching reaction mechanism is essential for the design and optimization of the etching process. However, the theoretical study of the etching mechanism is challenging due to the significant influence of crystallinity and impurities. Gas-phase etching of silicon nitride using hydrogen fluoride (HF) vapor provides an alternative to wet etching, particularly for addressing pattern-leaning issues in nanoscale structures. The etching process is continuous at elevated temperatures but exhibits self-limiting behavior at low temperatures [1]. Nevertheless, the atomic-scale mechanism remains poorly understood. Therefore, we performed density functional theory (DFT) calculations to study the etching mechanism [2]. Since silicon nitride films are typically amorphous with significant hydrogen impurities, we created an amorphous substrate model with a hydrogen concentration of 25 at.%. We then constructed four different slab models representing different degrees of fluorination and simulated fluorination pathways. All of the fluorination reactions were exothermic, but the activation energies varied. The cleavage of Si–N or Si–Si bonds and the release of byproducts showed low activation energies, indicating that etching would be plausible. We also simulated the formation and desorption of the $(NH_4)_2SiF_6$ salt on the fluorinated surface. The salt formation was also favorable due to low activation energies, which explains the self-limiting behavior of silicon nitride etching at low temperatures. However, at 152°C or higher, $(NH_4)_2SiF_6$ would decompose into gaseous byproducts, which explains the high etch rate at elevated temperatures. Our DFT calculation using the hydrogenated amorphous silicon nitride slab model successfully explained the etching of silicon nitride films by HF, which a crystalline Si_3N_4 slab model could not explain. Therefore, a slab model with the same composition and structure as the thin film to be etched is required to simulate the etching process.

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References [1] G. Vereecke and M. Meuris, EP1083592A1 (14 March 2001) [2] K. Khumaini et al., Appl. Surf. Sci. 654 (2017) 159414.

2:30pm **ALE-WeA-5 Dynamic Global Model of Cl_2/Ar Plasmas for Atomic Layer Etching of GaN**, ***Tojo RASOANARIVO****, C. Mannequin,* Nantes Université, CNRS, Institut des Matériaux de Nantes Jean ROUXEL, France; *F. ROQUETA, M. BOUFNICHEL,* STMicroelectronics, France; *A. RHALLABI,* Nantes Université, CNRS, Institut des Matériaux de Nantes Jean ROUXEL, France

Plasma Atomic Layer Etching (ALE) is an etching cyclic process. One ideal ALE cycle consists of two self-limited half reactions, separated by purge: an adsorption step to modify the uttermost surface layer and an activation step to selectively remove the modified layer without etching the underneath non-modified layers with an atomic scale resolution. ALE of GaN by alternating Cl_2 and Ar plasma, for the adsorption and activation steps, respectively, has been extensively studied [1]. In these processes, adsorption step is believed to rely on surface modification by chlorine radicals while activation is achieved by selectively controlling the energy of an ionic bombardment. However, these studies mostly focus on experimental approaches and modelling investigations are scarce.

As ALE is atomically sensitive, to better understand plasma/surface interactions at atomic scale, we must first precisely investigate plasma dynamics during the change from Cl_2 to Ar plasma corresponding to the transition from the adsorption to activation step. To date, global models have been well implemented to determine the plasma composition at specific plasma reactor parameters, with good computational time effectiveness [2]. These global models were initially designed to describe plasmas in steady-state conditions [3] and without considering any time dependent variations of the feedgas.

In this work, we develop a dynamic global model for Cl_2/Ar plasmas that follows time evolution of the plasma over a complete ALE cycle by modelling feedgas switches and RF power variations. Our model allows the calculation of neutrals and ions densities evolution over time, especially during the dynamic feedgas switch from a Cl_2 to an Ar plasma. We investigate the effects of the operating conditions such as RF power, pressure and total feedgas flowrate on the evolution of species densities and electron temperature. Higher chlorine species densities can be attained during the Cl_2 to Ar transition compared with a pure Cl_2 plasma. Long residence times for Cl_x species open the question on how to precisely control the surface reactions in GaN ALE.

Références

[1] Mannequin, Vallée, Akimoto, Chevolleau, Durand, et al., Journal of Vacuum Science & Technology A, (2020)
[2] Hurlbatt, Gibson, Schröter, Bredin, Foote, Grondein, O'Connell, Gans, Plasma Processes and Polymers Volume14, Issue1-2 (2017)
[3] Chanson, Rhallabi, Fernandez, Cardinaud, Landesman, Journal of Vacuum Science & Technology A, (2013)

2:45pm **ALE-WeA-6 A Transient Surface Site Balance Model for Si-Cl2-Ar Atomic Layer Etching**, *J. Vella,* Princeton Plasma Physics Laboratory; ***David Graves,*** Department of Chemical and Biological Engineering Princeton University and Princeton Plasma Physics Laboratory **INVITED**

Plasma-assisted atomic-layer etching (ALE) processes have the potential to attain controlled substrate removal.[1] While ALE is used in industry, there is still a lack of fundamental understanding surrounding many aspects of the processes. Simulation and modeling can help fill knowledge gaps, which will lead to the development of more efficient ALE processes. Previously, we have focused on modeling Si-Cl2-Ar ALE using molecular dynamics (MD) simulations, which have been validated against experiments.[2-4] We use the results from the MD simulations to develop a transient surface site balance model inspired by the work of Gray et al.[5] and Chang et al.[6] Within the model, the Si substrate is divided into three regions: the top, the mixed, and the crystalline layers. The model considers both the chlorination (surface modification) and ion bombardment (removal) sub-steps. The model accounts for Si and Cl present in the top and mixed layers of the substrate and thus all etched and sputtered products. Mixing of Cl from the top layer into the underlying mixed layer is also modeled. It is shown that this model accurately reproduces MD and select experimental results. The transient site balance model provides an intuitive methodology for modeling ALE processes and can be generalized to more complex processes and materials.References[1] K. J. Kanarik, T. Lill, E. A. Hudson, S. Sriraman, S. Tan, J. Marks, V. Vahedi, and R. A. Gottscho, "Overview of Atomic Layer Etching in the Semiconductor Industry", J. Vac. Sci. Technol. A, 2015, 33, 020802.[2] J. R. Vella, D. Humbird, and D. B. Graves, "Molecular Dynamics Study of Silicon Atomic Layer Etching by Chlorine Gas and Argon Ions", J. Vac. Sci. Technol. B, 2022, 40, 023205.[3] J. R. Vella and D. B. Graves, "Near-Surface Damage. And Mixing in Si-Cl2-Ar Atomic Layer Etching Processes: Insights from Molecular Dynamics Simulations", J. Vac. Sci. Technol. A, 2023, 41, 042601.[4] J. R. Vella, Q. Hao, V. M. Donnelly, and D. B. Graves, "Dynamics of Plasma Atomic Layer Etching: Molecular Dynamics Simulations and Optical Emission Spectroscopy", J. Vac. Sci. Technol. A, 2023, 41, 062602.[5] D. C. Gray, I. Tepermeister, and H. H. Sawin, "Phenomenological Modeling of Ion-Enhanced Surface Kinetics in Fluorine-Based Plasma Etching", J. Vac. Sci. Technol. B, 1993, 11, 1243-1257.[6] J. P. Chang, J. C. Arnold, G. C. H. Zau, H. Shin, and H. H. Sawin, "Kinetic Study of Low Energy Argon Ion-Enhanced Plasma Etching of Polysilicon with Atomic/Molecular Chlorine", J. Vac. Sci. Technol. A, 1997, 15, 1853-1863.

3:15pm **ALE-WeA-8 Theoretical Analysis on Halogenation of Transition Metal Surfaces toward Thermal Atomic Layer Etching**, ***Hyun Cho****, M. Kim, B. Shong,* Hongik University, Republic of Korea

In fabrication of the semiconductor devices involving three-dimensional structures with shrinking sizes, challenges in etching processes are being emphasized, such as roughness and selectivity issues. Atomic layer etching (ALE) is a possible alternative etching technology that removes small designated amount of material per process step in a self-limiting manner, resulting in precise control over the etch thickness and reduced roughness. Especially, in order to enable isotropic etch processes at the inner surfaces of three-dimensional substrates, thermal ALE processes comprised entirely of reactions of neutral reactant molecules are desirable. Many recent reports on thermal ALE utilize halogenation reaction at either conversion or volatilization steps. Since such surface reactions strongly depend on the substrate materials and halogenation reactants, it is desirable to identify the reactivity of possible self-limiting halogenation according to the reactant-substrate combinations. In this study, we conducted an analysis on the energetics of the surface halogenation of some transition metal surfaces, using density functional theory (DFT) and machine learning potential (MLP) calculations. By calculating the adsorption energy of Cl and F atoms depending on their surface coverage, as well as the energy change in conversion into metal halide overlayers, the spontaneity according to the degree of halogenation could be compared. The different reactivities of several molecular chlorination and fluorination agents, such as Cl_2, F_2, $SOCl_2$, and SF_4, are also compared.

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